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This Final Technical Report covering the three-year period from December 1, 1990 to November 30, 1993 presents a summary of research performed on two classes of materials obtained by the sol-gel method. Single crystal thin films were successfully prepared for the ferroelectric materials $KNbO_3$ and $LiNbO_3$. A new phenomenon, *Amorphous Ferroelectricity was discovered.* Organically Modified Silicates (Ormosils) were further developed to give enhanced high temperature rubbery elasticity. A theory was developed for the calculation of the hardness of Ormosils. By modifying the Ormosils with Ti, Zr and Al to replace Si, Vickers Hardness of over 200 Kg/mm^2 was obtained. This is about ten times that of the hardness of the hardest transparent organic plastics.

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ABSTRACT

This Final Technical Report covering the three-year period from December 1, 1990 to November 30, 1993 presents a summary of research performed on two classes of materials obtained by the sol-gel method. Single crystal thin films were successfully prepared for the ferroelectric materials $KNbO_3$ and $LiNbO_3$. A new phenomenon, *Amorphous Ferroelectricity was discovered.* Organically Modified Silicates (Ormosils) were further developed to give enhanced high temperature rubbery elasticity. A theory was developed for the calculation of the hardness of Ormosils. By modifying the Ormosils with Ti, Zr and Al to replace Si, Vickers Hardness of over 200 Kg/mm^2 was obtained. This is about ten times that of the hardness of the hardest transparent organic plastics.

1. Introduction

In a previous AFOSR-funded research program directed by J.D. Mackenzie at UCLA (AFOSR Grant No. 88-0066), which was related to new materials based on the sol-gel processing method, significant progress was made in a number of thrust areas. The first one was concerned with the preparation of ferroelectric thin films. The second one was on the preparation of some entirely new organic-inorganic hybrid materials known as "ORMOSILS" (Organically modified silicates). The present project that was concluded on November 30, 1993 (AFOSR-91-0096) was essentially a continuation of work under AFOSR-88-0066. In the past three years, research has been continued at UCLA on ferroelectrric thin films and Ormosils. This report technical report covers research conducted at UCLA under J.D. Mackenzie from December 1, 1990 to November 30, 1993.

2. Research Progress in Ferroelectric Films

(a) Crystalline Films

On progress made in the preparation of polycrystalline ferroelecric thin films and knowledge gained on the structure and properties of sol-gel liquid solutions, we were able to prepare single crystal films of LiNbO3 on a $LiTaO_3$ substrate in December, 1990. This was achieved through precise control of the chemistry and hence the structure of the sol-gel liquid solutions. The high-resolution electron microscopy results on a $LiNbO_3$ film is shown in Fig. 1. We were then able to exploit this technique for the growth of $KNbO_3$ single crystal films on $SrTiO_3$ substrates. The lattice fringe image and electron diffraction of a $KNbO_3$ single crystal film are shown in Fig. 2. The technique was also successfully applied to the growth of single crystal $PbTiO_3$ film on $SrTiO_3$. The optical properties of these films have been measured. We have also succeeded in growing up to twelve alternating layers of $PbTiO_3$ and $SrTiO_3$, that is, six pairs. These films will be evaluated for quantum well applications.

Another significant development in this period is the discovery by our group of ferroelectricity in α-Nb_2O_5 and γ-Nb_2O_5. These compounds are fairly common but there was no mention of their ferroelectric property in the literature. From structural considerations, we concluded that Nb_2O_5 should exhibit ferroelectric behavior and indeed this way found to be true. The ferroelectric

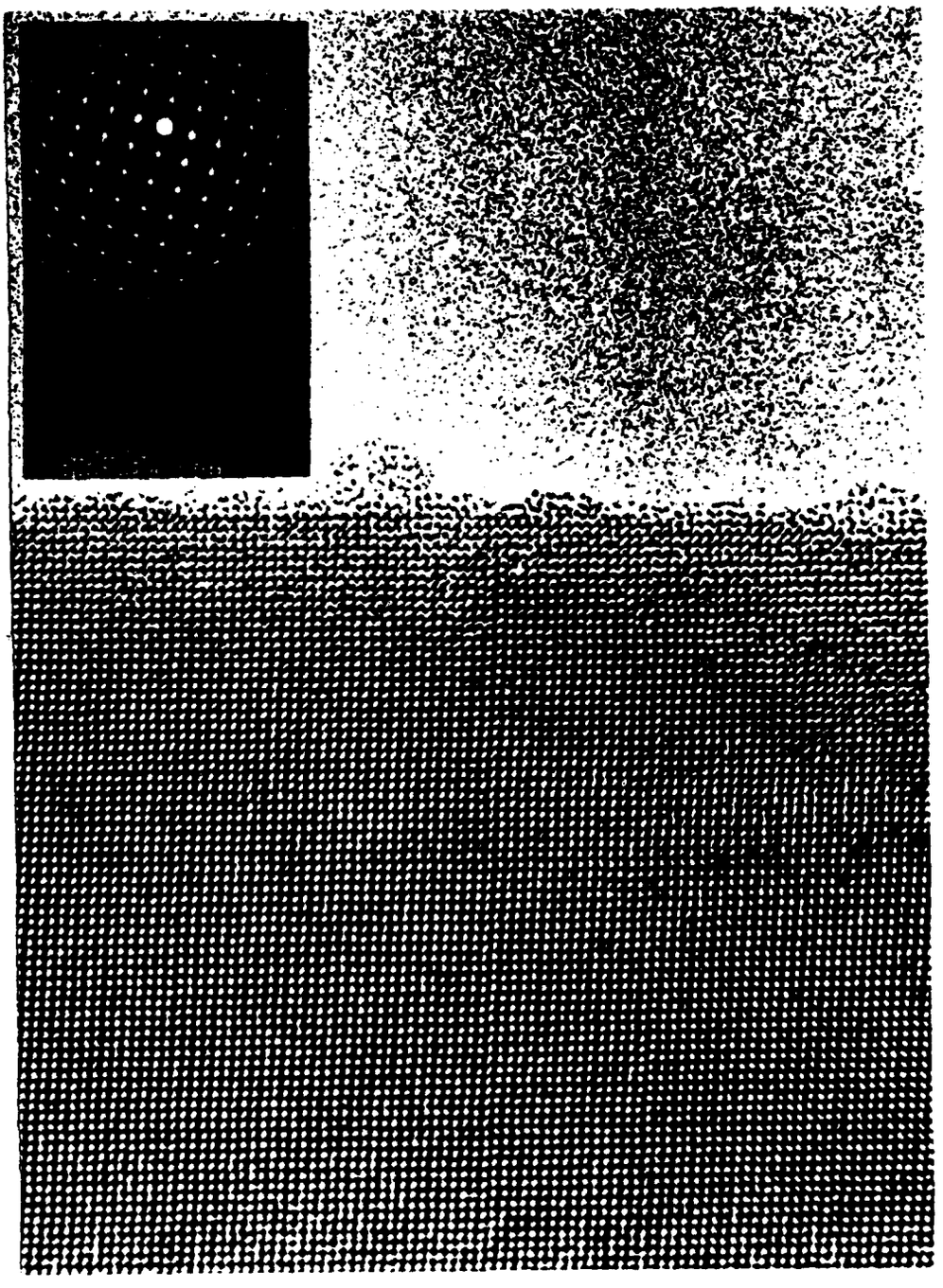


Fig. 1 High-resolution electron microscopy picture of single crystal film of $LiNbO_3$ on $LiTaO_3$ substrate showing the lattice fringe and electron diffraction pattern.

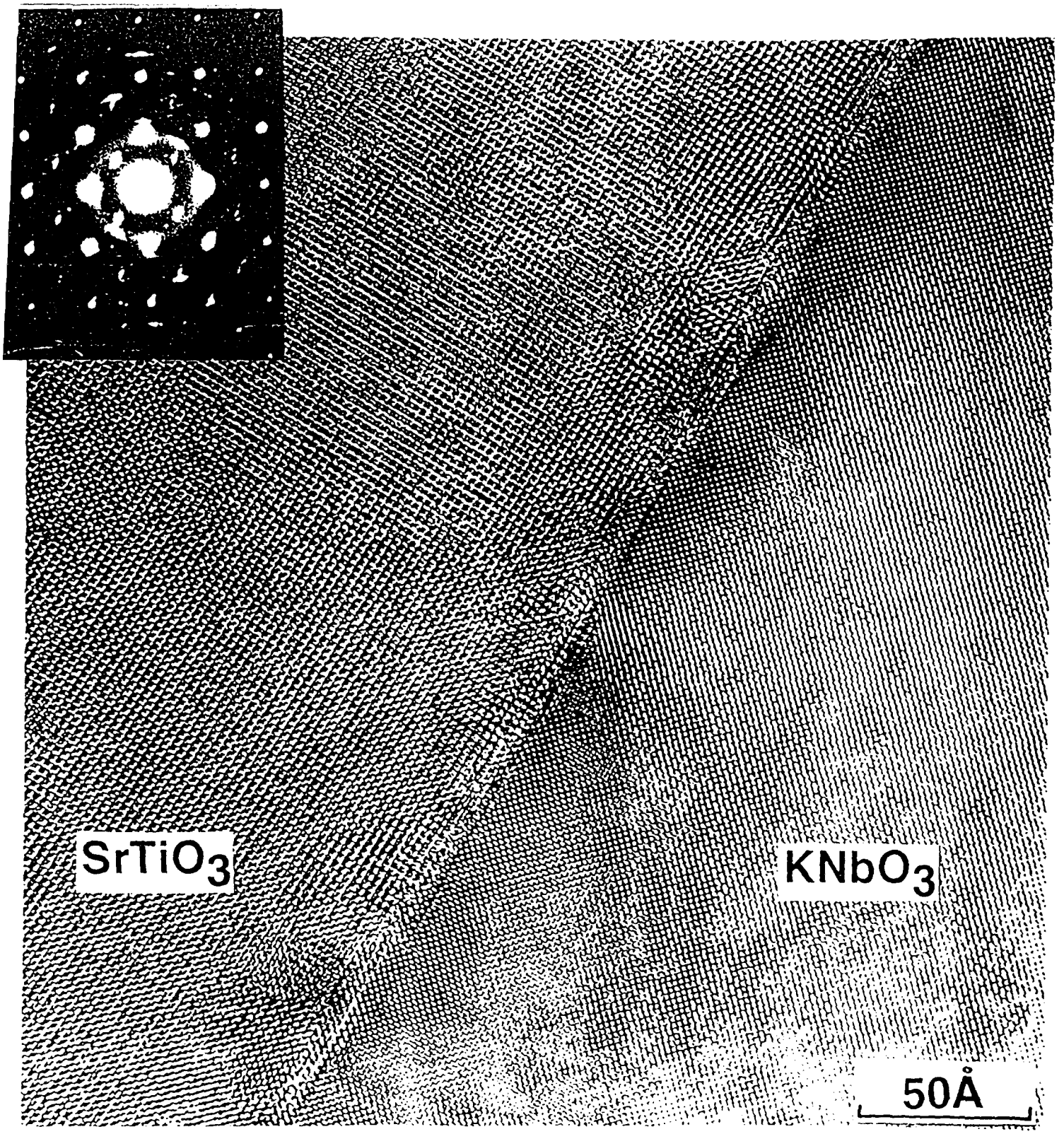


Fig. 2 Lattice fringe image and electron diffraction of epitaxial single crystal $KNbO_3$ *film grown on single crystal* $SrTiO_3$ *substrate by the sol-gel processing.*

hysteresis loops for Nb_2O_5 are shown in Fig. 3. A comparison of γ-Nb_2O_5 with other ferroelectrics is presented in Table 1. This is the first and only example of a single component oxide now known to be ferroelectric. Thin films of Nb_2O_5 have been prepared from sol-gel solutions.

(b) Amorphous Ferroelectric Films

The sol-gel process for the preparation of films involves the deposition of a liquid solution on to a substrate. The solid film first formed at room temperature is invariably amorphous. Subsequent heating to high temperatures, usually above 350°C, causes the amorphous film to crystallize. In our work to prepare single crystal films of $LiNbO_3$, the structural species in the sol-gel solution are assumed to be very similar to that in the crystal. Thus, it would seem logical to expect that the structural species in the amorphous film would also resemble those in the crystal. Although all established theories suggest that ferroelectricity is the sole property of some crystalline solids, there were no theories which suggested that ferroelectricity cannot occur in amorphous solids. We therefore proceeded to investigate the properties of our amorphous $LiNbO_3$ films. We discovered that the amorphous $LiNbO_3$ exhibited ferroelectric behavior. This was confirmed for PZT $BaTiO_3$, $KNbO_3$ and SBN on a variety of substrates including organic polymers. The P-E hysteresis loops of crystalline and amorphous $LiNbO_3$ are shown in Fig. 4. Although the remanent polarization of the amorphous film is significantly less than that of the crystalline film, 7.8 vs. 110 $\mu c/cm^2$, the spontaneous polarization of the amorphous film is confirmed. A tentative model has been postulated for the origin of ferroelectricity in the amorphous films. Small domains labeled "Ferrons" are suggested to be present as shown in Fig. 5.

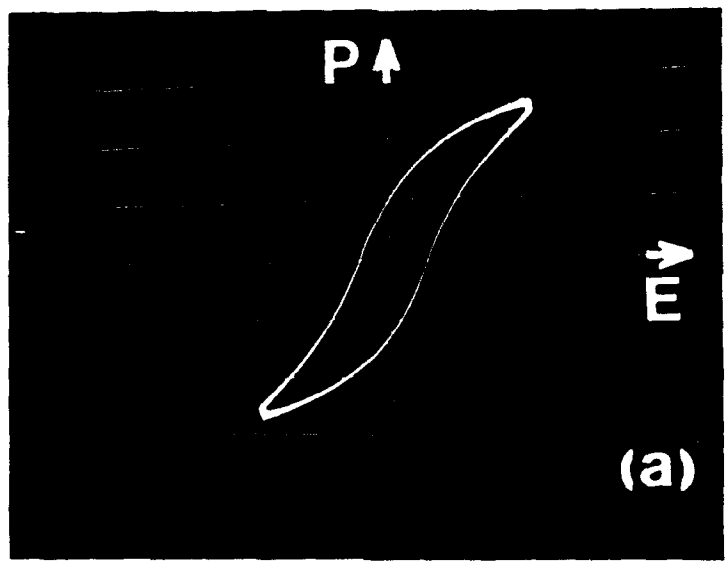
3. Research Progress in Organically Modified Silicates (Ormosils)

By reacting tetraethoxysilane (TEOS) and polydimethylsiloxane (PDMS) in alcoholic solutions and controlling the reaction via catalysts, temperature and time, we were able to control the microstructures of the gels formed. The properties of these ORMOSILS varied from hard and transparent to rubbery and opaque. The hardest ORMOSILS made had a Vickers Hardness of about 175

Table 1 Properties of γ-Nb_2O_5 compared with other ferroelectric niobates (at room temperature)

	γ-Nb_2O_5	$LiNbO_3$	$KNbO_3$	$Sr_{1-x}Ba_xNb_2O_6$	$Ba_2NaNb_5O_{15}$	$Sr_2Nb_2O_7$
Structure Type	α-UO_3	$LiNbO_3$	Perovskite	Tungsten-Bronze	Tungsten-Bronze	$Sr_2Nb_2O_7$ Family
Point Group (RT)	mm2	3m	mm2	4mm	mm2	2
Curie Point (°C)	860 (un-certain)	1210	435	40-160	560	1342
Polarization ($\mu C/cm^2$)	8 (P_r)	70 (P_s)	30 (P_s)	32 (P_s)(x = 0.4)	40 (P_s)	9 (P_s)
Pyroelectric Coefficient (nC/cm^2)	8.6	4	--	70 (x = 4)	--	--
Relative			120 (K_{11})		246 (K_{11})	75 (K_{11})
Dielectric		75 (K_{11})	1200 (K_{22})	500 (K_{33})	242 (K_{22})	46 (K_{22})
Permittivity	7*	30 (K_{33})	40 (K_{33})	(x = 0.5)	51 (K_{33})	43 (K_{33})

* Data measured with sandwiched powder samples at 1 volt and 100 kHz. Sample thickness ≈ 0.47 mm.



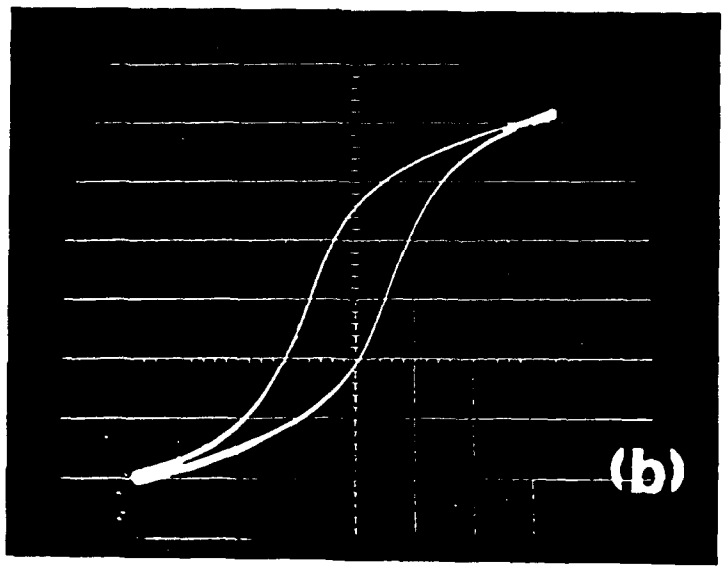
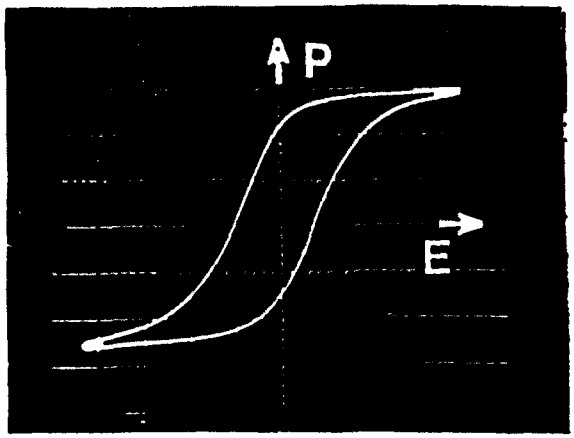
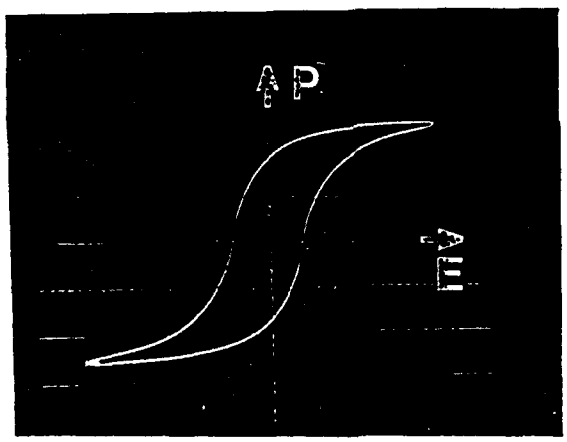


Fig. 3 P-E Hysteresis loops of (a) γ-Nb_2O_5 powder and (b) α-Nb_2O_5 powder



P-E hysteresis loop (at 60Hz) in the Pt(electrode)/$LiNbO_3$ thin film/ Au(electrode) sample with sandwich structure made by the sol-gel technique (450°C/5h, film thickness is 1300Å). The remanent polarization P_r is 110μC/cm^2 and the coercive field E_C is 23 kV/mm were observed from the loop.



P-E hysteresis loop (at 60Hz) of amorphous $LiNbO_3$ thin film (120°C/2h) coated on gold passivated silicon wafer with platinum top electrode. The remanent polarization P_r is 7.8μC/cm^2 and the coercive field E_C is 11 kV/mm were observed from the loop.

Fig. 4 P-E Hysteresis Loops of $LiNbO_3$

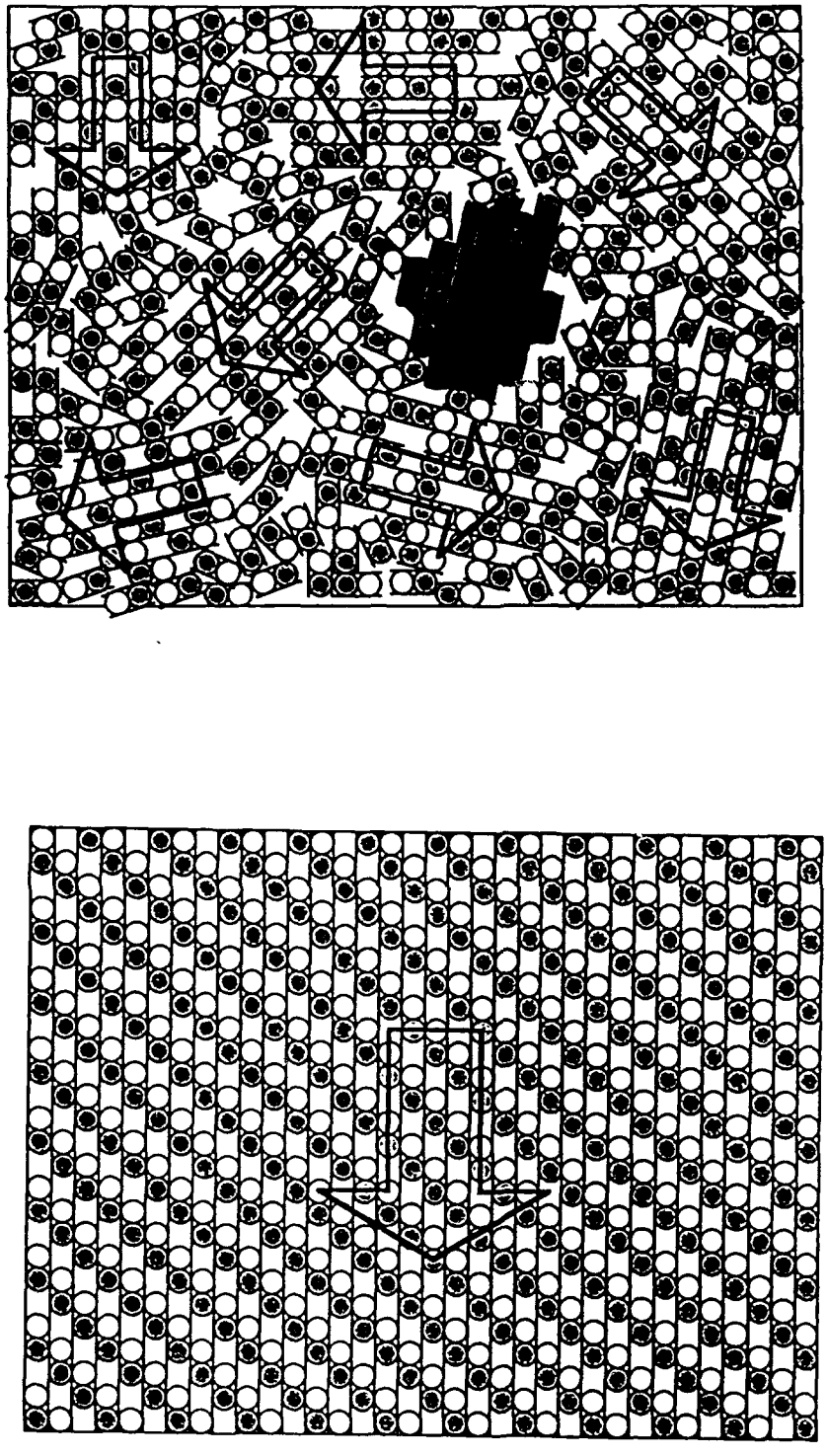


Fig. 5 A two-dimensional representation of the domain structure of a crystal (**top**) and an amorphous film (**bottom**)

Kg/mm^2 which is very much harder than the hardest organic plastics and approaches the hardness of phosphate glasses. Some samples of the rubbery ORMOSILS are shown in Fig. 6. These rubbery ORMOSILS are unique in many ways.

A tentative model has been developed to explain the rubbery behavior on the basis of ^{29}Si NMR studies and mechanical properties measurement. The structure of a rubbery Ormosil is shown schematically in Fig. 7. Under external compression, for instance, the PDMS chains which link the SiO_2 islands can coil-up via the rotation of the Si-O-Si bonds because the Si-O-Si angles are approximately 150°. On stress release, the PDMS chains would uncoil. Thus, the brittle SiO_2 islands would not be subjected to failure stresses.

The rubbery ORMOSILS are unique in that they can contain some 80% by weight of SiO_2 and still retain their rubbery behavior. By using polydimethyldiphenyl silaxane instead of PDMS, the thermal stability of ORMOSILS is enhanced. Commercial antioxidants can also be added to enhance thermal stability. Some results are shown in Figs. 8 and 9.

A theory has been developed or the calculation of Vickers Hardness of ORMOSILS. The use of ultrasonic irradiation to improve hardness based on tighter packing of the sols was investigated. Figure 10 shows the method of calculation and Figure 11 a comparison of theoretical and experimental results. Our theory suggests that the partial substitution of SiO_2 with TiO_2, Al_2O_3 and ZrO_2 can further increase the hardness. Preliminary confirmation with TiO_2 is shown in Figure 12.

When Ormosil samples are heated to temperatures in the range of 800-1000°C in an inert atmosphere (N_2 or Ar), the samples would turn into a black colored porous ceramic with retention of shape. This heat-treated sample can now be heated in air up to 1200°c with retention of shape as well as the black color. ^{13}C CPMAS NMR, ^{29}SiCPMAS NMR, X-ray, and electron microscopy studies revealed that an oxycarbide phase is formed. The expansion coefficient of the porous ceramic is extremely low. These materials could become a new family of refractory insulating ceramics. The proposed microstructure of these new nanocomposites is shown in Figure 13.

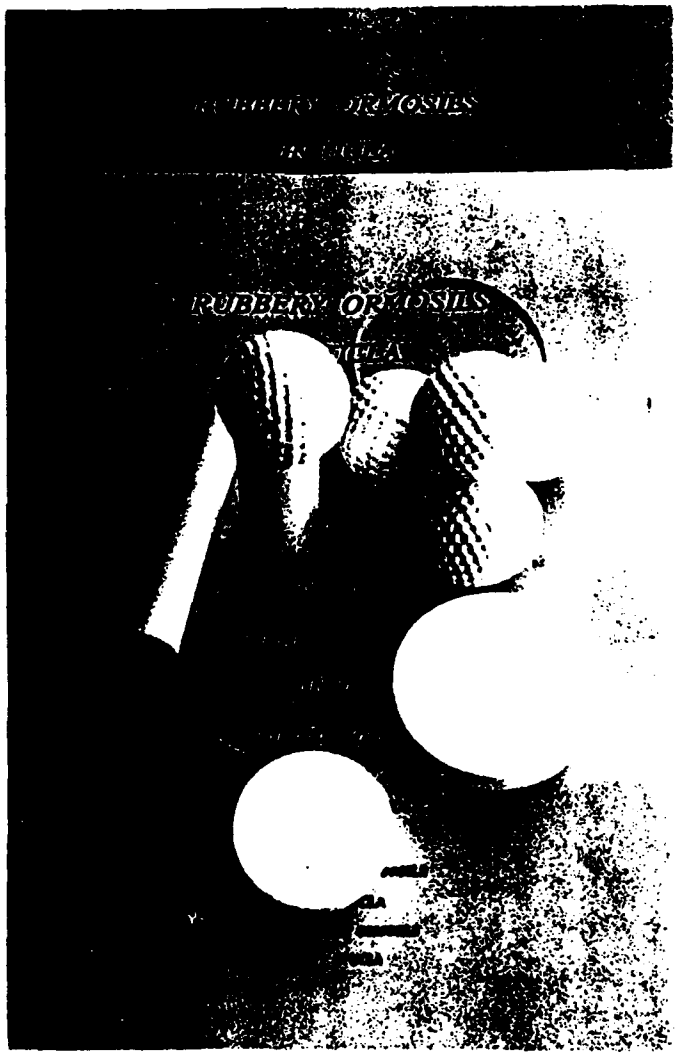


Fig. 6 Examples of Rubbery Ormosils

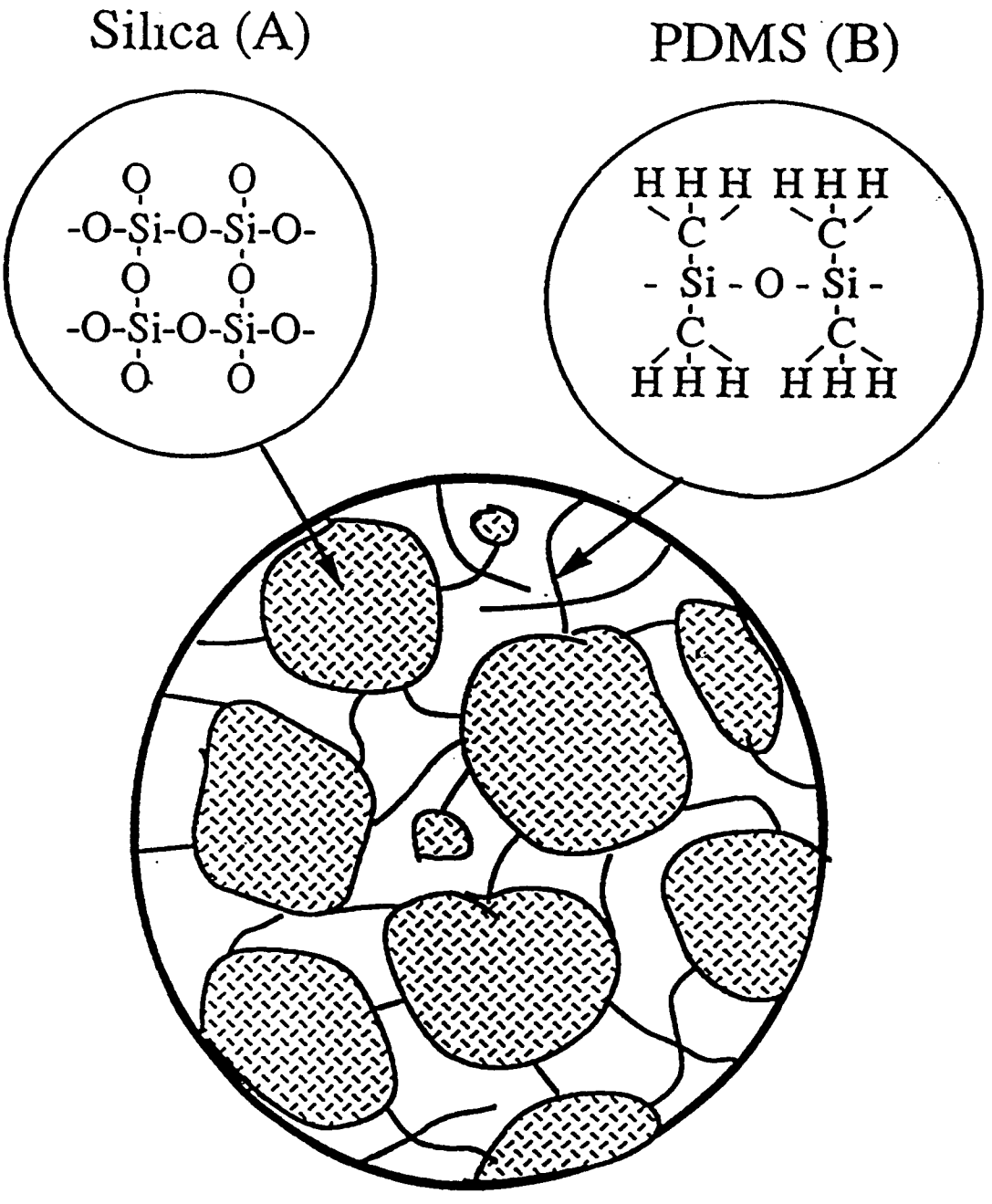
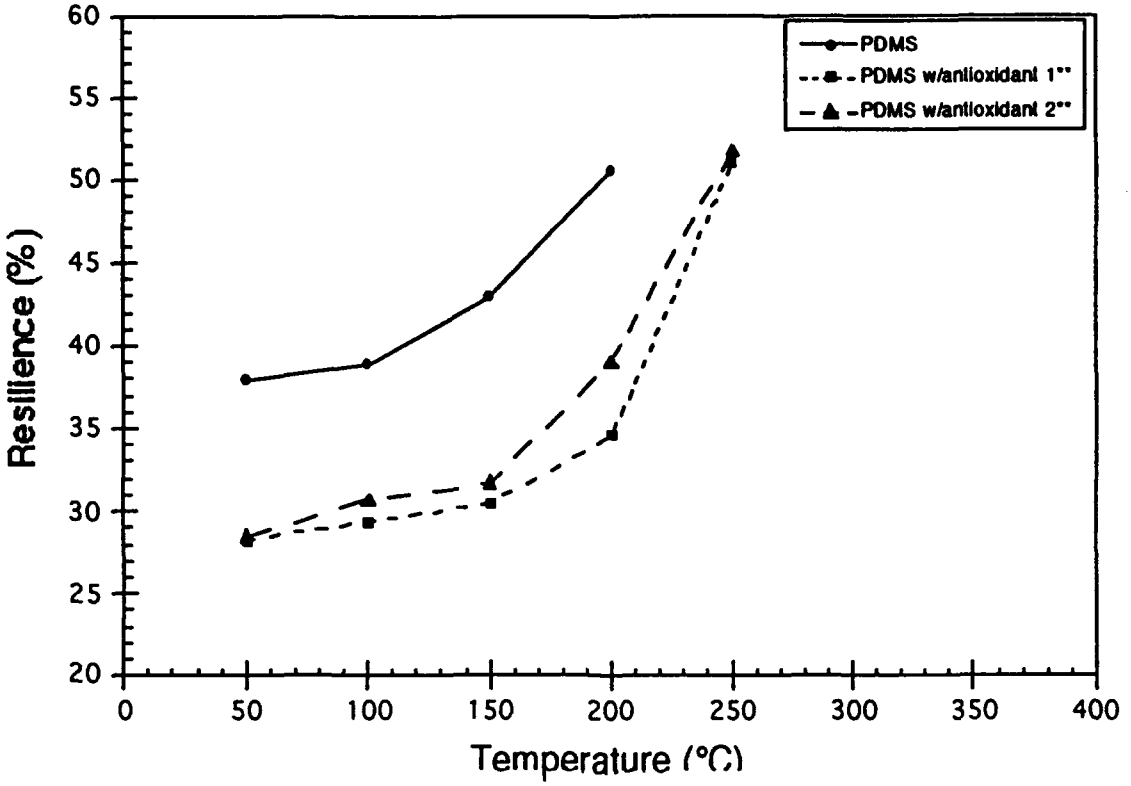
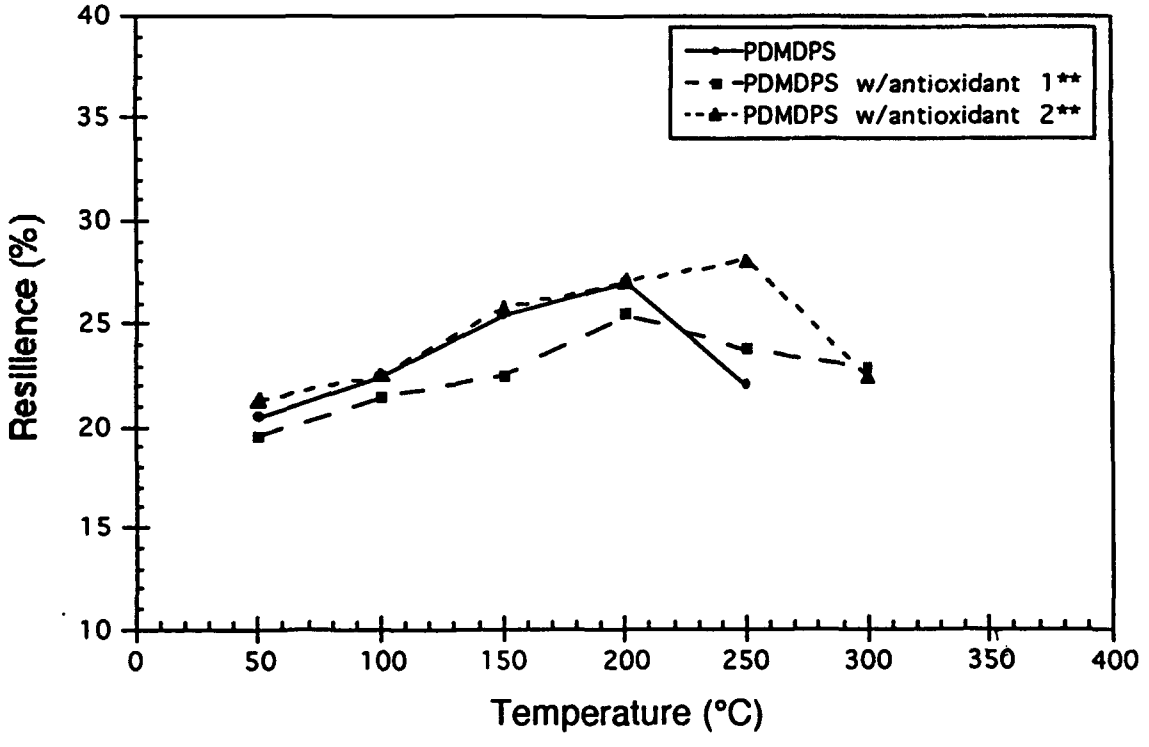


Fig. 7 **Schematic illustration of the structure of Ormosils.**

Fig. 8 Ormosil Resilience

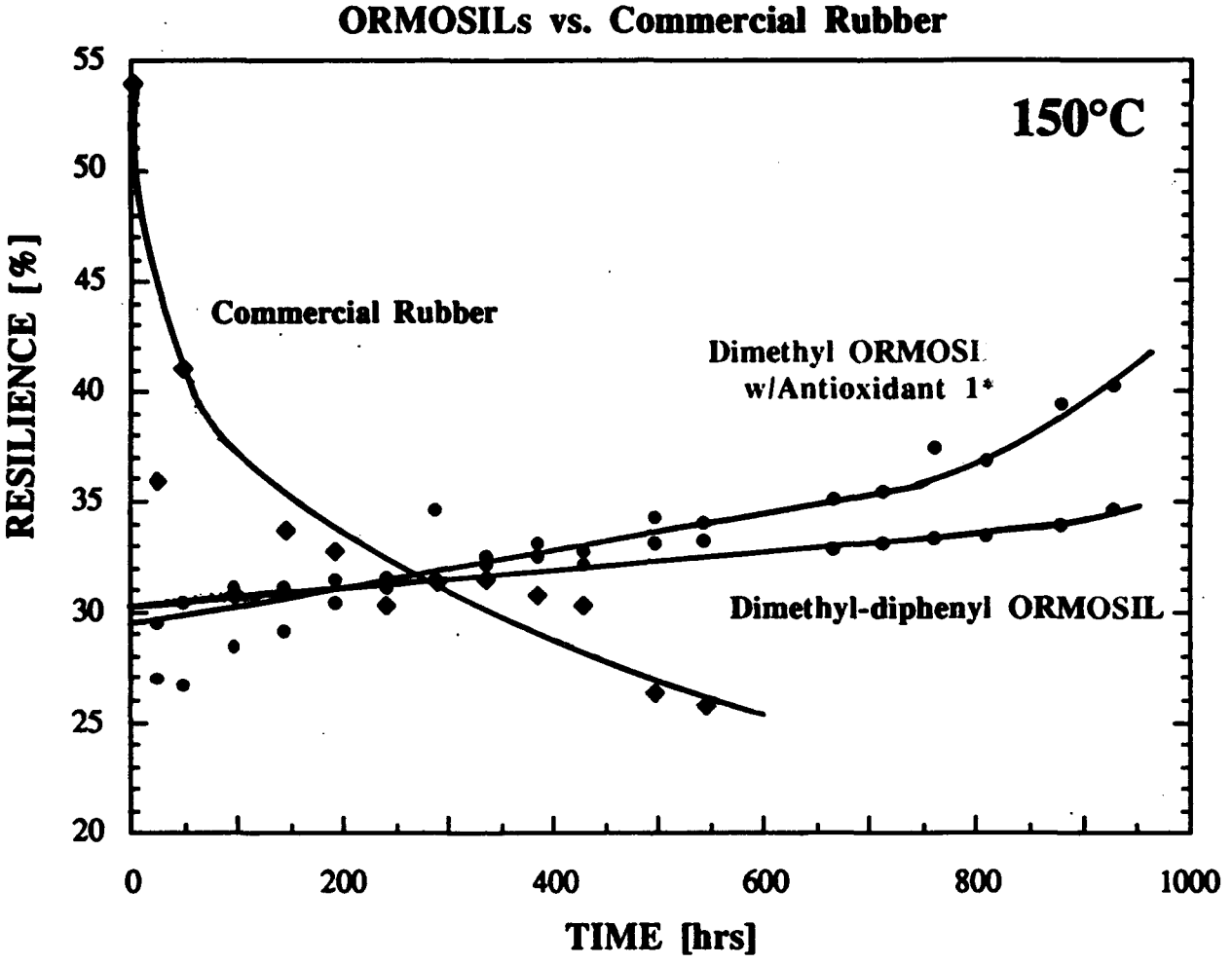




All samples held at constant temperature for 24 hrs.

** Antoxidant 1: Naugard 445; Antoxidant 2: Wingstay 29 (Polyphenylamines)

Fig. 9 Comparative Resilience



Resilience Comparison of ORMOSILs vs. Rubber as a function of time at a constant temperature of 150°C.

- Rubber initially loses resiliency, then exterior becomes brittle and cracks due to oxidation until resilience is no longer obtainable.
- ORMOSILs retain resilience to at least 1000 hrs at 150°C.
- Chemical modification (dimethyl-diphenyl) retards increase in resilience of ORMOSILs with heat treatment.

* Naugard 445, Uniroyal Chemical

Fig. 10 Calculation of Vickers hardness of sono-Ormosils

$$H_V = 0.395C[1/(10.8V_t-1)]^{1/2}V_t^2\alpha^{1/2}G \qquad (1)$$

where C is a constant, V_t is the packing density, α is the relative bond strength (α=1 for silica glass), and G is the dissociation energy per unit volume.

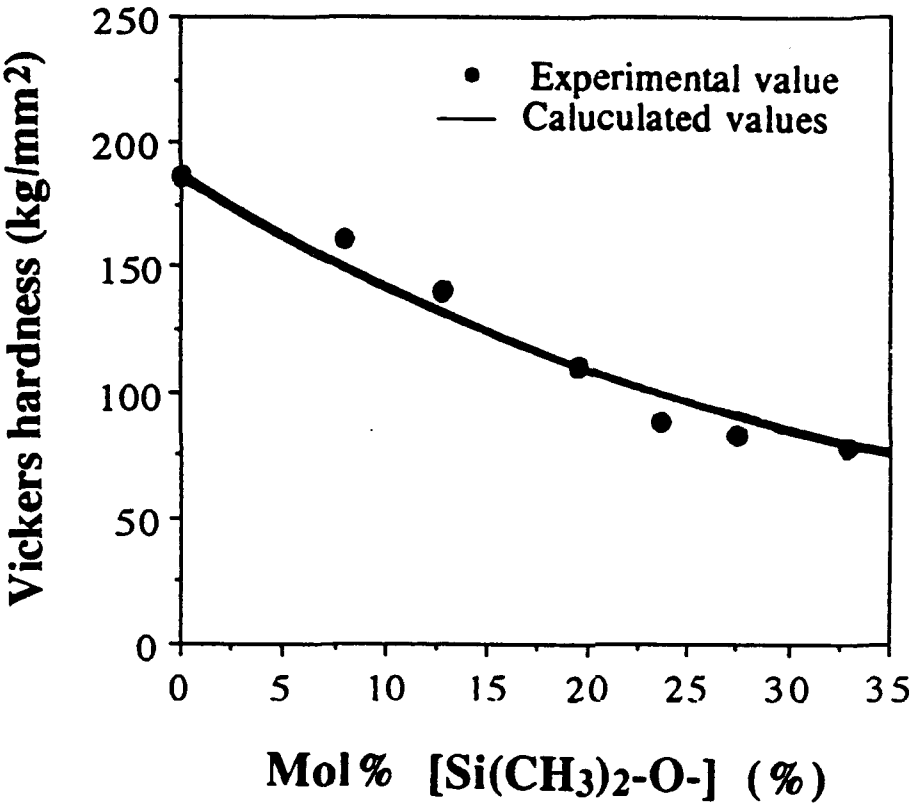
H_V increases with increasing V_t and is proportional to $\alpha^{1/2}G$.

α, G and $\alpha^{1/2}G$ for various oxides

Oxide	CN*	α	G (kcal/cm^3)	$\alpha^{1/2}G$
Al_2O_3	4	0.953	32.0	31.24
	6	0.632	32.0	25.44
ZrO_2	4	1.142	23.2	24.79
	6	0.762	23.2	20.25
	8	0.572	23.2	17.55
TiO_2	4	1.028	20.7	20.99
	6	0.684	20.7	17.12
SiO_2	4	1.000	15.4	15.40

*CN stands for coordination number.

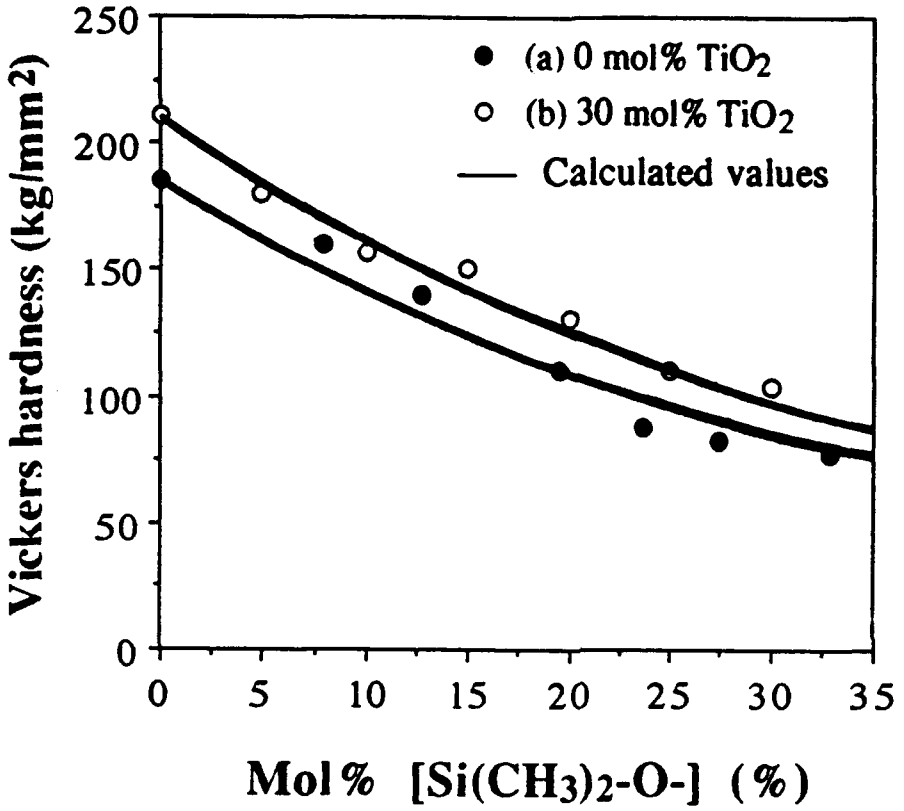
Fig. 11 Vickers hardness of sono-Ormosils



Vickers hardness of the hardest transparent plastics and some glasses

Material	Vickers hardness (kg/mm²)
Polyethyleneterephthalate (PET)	24
Polymethylmethacrylate (PMMA)	19
Polycarbonate (PC)	14-16
Borosilicate glass	220-350
Window glass	480-620

Fig. 12 Vickers hardness of sono-Ormosils



(a) SiO_2 as an oxide component

(b) SiO_2 + 30 mol % TiO_2 as an oxide component

Our equation (1) suggests that adding TiO_2, ZrO_2 or Al_2O_3 to an ormosil can further increase Vickers hardness.

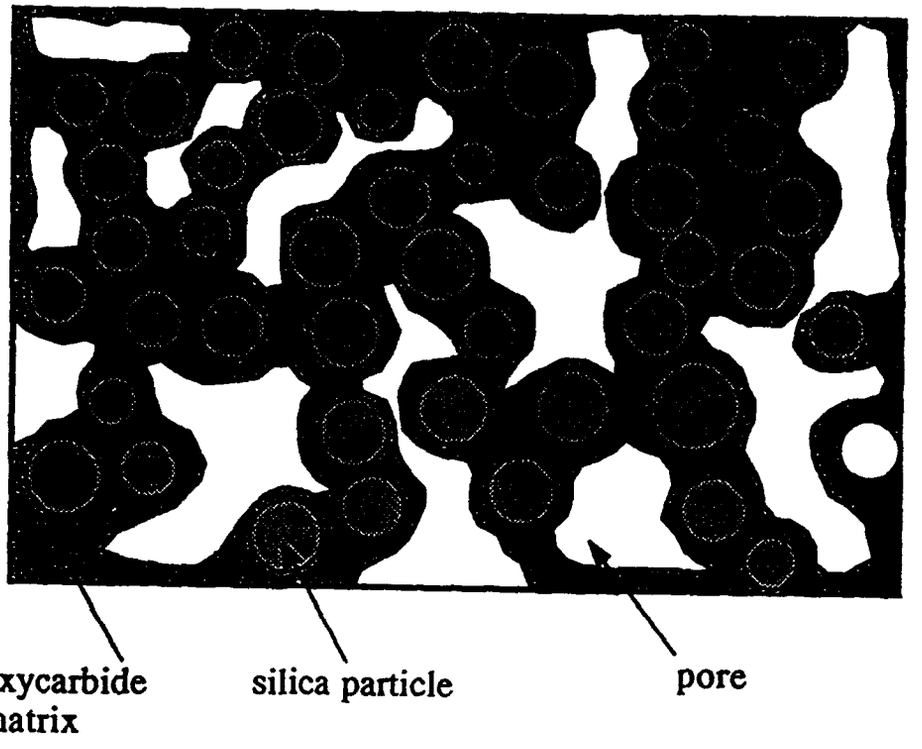


Fig. 13 The final black ceramic consists of silica particles covered with an oxycarbide-matrix in which carbon atoms are cross-linked to other carbon atmos or silicon. This mateial contains numerous large pores which are responsible for the extremely light weight of the samples. Figure 24 illustrates the porous black ceramic microstructure.

4. Cumulative Publications form this Grant

1. J. Heo, J.S. Sanghera and J.D. Mackenzie, *Chalcohalide Glasses for Infrared Fiber Optics*, Opt. Engineering, 30 (1991) 470-479.

2. F. Hulderman, J.S. Sanghera and J.D. Mackenzie, *The Effect of UV Radiation on the Mechanical Strength of As_2Se_3 Glass Fibers*, J. Non-Cryst. Solids, 127 (1991) 312-322.

3. C.J. Chen, Y.H. Xu, R. Xu and J.D. Mackenzie, *Ferroelectric and Pyroelectric Properties of Strontium Barium Niobate Films Prepared by the Sol-Gel Method*, J. Appl. Phys. 69 (1991) 1763-1765.

4. Y.H. Xu, C.J. Chen, R. Xu and J.D. Mackenzie, *Ferroelectric $Sr_{0.60}Ba_{0.40}N_2O_6$ Thin Films by Sol-Gel Process: Electrical and Optical Properties*, Phys. Rev. B, 44 (1991) 35-41.

5. J.D. Mackenzie, C.Y. Li and Y.H. Xu, *Glasses as Nonlinear Optical Materials*, Chemistry Express, 6 (1991) 903-920.

6. J.D. Mackenzie, *Advanced Ceramics from Liquid Solutions*, **Ceramics: Toward the 21st Century**, Ed. by N. Soga and A. Kato, Ceram. Soc. of Japan (1991) 597-611.

7. Y.H. Xu, **Ferroelectric Materials and Their Applications** (a book), North-Holland, The Netherlands (1991).

8. C.H. Cheng, Y.H. Xu and J.D. Mackenzie, *Photoelectric Properties of Undoped and Fe-Doped $LiNbO_3$ Films made by Sol-Gel Method*, MRS Symp. , 243 (1991) 551-556.

9. J.D. Mackenzie, H.X. Zheng and M.W. Colby, *Glasses for Electronic Applications: Why and What*, Ceramic Trans., Ed. by K.M. Nair, 20 (1991) 345-355.

10. C.J. Chen, Y.H. Xu and J.D. Mackenzie, *Ferroelectric Thin Flms by Sol-Gel Processing*, J. Wave-Materials Interaction (1991) in press.

11. F. Kirkbir, J.D. Mackenzie, *Lead Oxide Fine Particles from Lead Nitrate Solution*, J. Matls. Sci. 27 (1992) 1748-1756.

12. J.D. Mackenzie, Y.J. Chung and Y. Hu, *Rubbery Ormosils and Their Applications*, J. Non-Cryst. Solids, 147/148 (1992) 271-279.

13. R. Xu, Y.H. Xu and J.D. Mackenzie, *Low Temperature Processing of Ferroelectric Thin Films and Amorphous Ferroelectricity*,

Ferroelectrics (accepted for publication as **Proc. 3rd Intl Symp. on Integrated Ferroelectrics,** Colorado Springs, Colorado, April 2-5, 1992).

14. Y. Hu an J.D. Mackenzie, *Rubber-Like Elasticity of Organically Modified Silicates*, J. Mat. Sci. 27 (1992) 4415-4420.

15. J.D. Mackenzie, R. Xu and Y.H. Xu, *Ultrastructure Processing of Thin Crystalline Films*, **Chemical Processing of Advanced** Materials, Eds. L.L. Hench, J.K. West, Wiley, N.Y. (1992) 365-377.

16. S.J. Kramer, M.W. Colby, J.D. Mackenzie, B.R. Matles, R.B. Kaner, *Polyailine-Ormosil Nanocomposites*, **Chemical Processing of Advanced Materials**, Ed. L.L. Hench, J.K. West, Wiley, N.Y. (1992) 737-744.

17. Y.H. Xu and John D. Mackenzie, *Ferroelectric Thin Films Prepared by Sol-Gel Processing*, Integrated Ferroelectrics, 1 (1992) 17-42.

18. Y.H. Xu, C.H. Cheng, R. Xu and J.D. Mackenzie, *Electrical Properties of Crystalline and Amorphous* $Pb(Zr_xTi_{1-x})O_3$ *Thin Films Prepared by the Sol-Gel Technique*, MRS Symp. Proc., 271 (1992) 359-364.

19. C.H. Cheng, Y.H. Xu, J.D. Mackenzie, J. Zhang and LeRoy Eyring, *The Growth of Single Crystal-Like and Polycrystal* $KNbO_3$ *Films via Sol-Gel Process*, MRS Symp. Proc., 271 (1992) 383-388.

20. R. Xu, Y.H. Xu and J.D. Mackenzie, *Amorphous Thin Films of Ferroelectric Oxides*, SPIE Proc., 1758 (1992) 261-273.

21. C.H. Cheng, Y.H. Xu and J.D. Mackenzie, *Second-Harmonic Generation in Metal Oxide/Ormosils Nanocomposites from Sol-Gel Method*, SPIE Proc., 1758 (1992) 485-491.

22. J.D. Mackenzie, *Ultrastructure Processing of Shaped Ceramic Bodies from Liquids*, **Ultrastructure Processing of Advanced Materials**, Ed. Dr. R. Uhlmann, D.R. Ulrich, Wiley, N.Y. (1992) 121-133.

23. A Nazeri-Eshghi, J.D. Mackenzie, *Densification of Silica-Cubic Boron Nitride Composites*, **Ultrastructure Processing of Advanced Materials**, Ed. D.R. Uhlmann, D.R. Ulrich, Wiley, N.Y. (1992) 393-400.

24. H. Zheng, J.D. Mackenzie, *A Novel Process for Fabrication of High* T_c, *Superconductors, A Glass-to-Ceramic Process*, **Ultrastructure Processing of Advanced Materials**, Ed. D.R. Uhlmann, D.R. Ulrich, Wiley, N.Y. (1992) 629-640.

25. C.H. Li, J.Y. Tseng, K. Morita, C. Lechner, Y. Hu, J.D. Mackenzie, *Ormosils as Matrices in Inorganic-Organic Nanocomposites for Various Optical Applications*, SPIE Proc., 1758 (1992) 410-419.

26. J.Y. Tseng, C.Y. Li, T. Takada, C. Lechner, J.D. Mackenzie, *Optical Properties of Metal Cluster-Doped Ormosil Nanocomposites*, SPIE Proc., 1758 (1992) 612-620.

27. J.D. Mackenzie, *Sol-Gel Optics II* editor, SPIE, Bellingham, Washington (1992).

28. J.D. Mackenzie, *Nonlinear Optical Materials by the Sol-Gel Method*, J. Sol-Gel Sci. & Tech., 1 (1993) 7-19.

29. J.D. Mackenzie, *Sol-Gel Optics*, J. Ceram. Soc. Japan, 101 (1993) 1-10.

30. H.T. Lin, E. Bescher, J.D. Mackenzie, H. Dai, O.M. Stafsudd, *Preparation and Properties of Laser Dye-Ormosil Composites*, J. Matls. Sci., 27 (1992) 5523-5528.

31. Y. Hu and J.D. Mackenzie, *Structure-Related Mechanical Properties of Ormosils by Sol-Gel Process*, MRS, 271 (1992) 681-686.

32. K. Morita, Y. Hu and J.D. Mackenzie, *The Effect of Ultrasonic Radiation on Gelation and Properties of Ormosils*, MRS Symp. Proc., 271 (1992) 693-698.

33. Y.H. Xu, C.H. Cheng, R. Xu, J.D. Mackenzie, *Electrical Properties of Amorphous Thin Films of Ferroelectric Oxides Prepared by Sol-Gel Technique*, MRS Symp. Proc., 310 (1993) 441-446.

34. E.J.A. Pope and J.D. Mackenzie, *Sol-Gel Processing of Neodymia-Silica Glass*, J. Am. Ceram. Soc., 5 (1993) 1325-1328.

35. T. Iwamoto, K. Morita, J.D. Mackenzie, *Liquid State ^{29}Si NMR Study on Sol-Gel Reaction Mechanisms of Ormosils*, J. Non-Cryst. Solids, 159 (1993) 65-72.

36. J.D. Mackenzie, H. Zheng, *Oxide-Non Oxide Glasses*, Proc. XVI Int. Congress on Glass, 1 (1993) 1-23.

37. A. Nazeri, E. Bescher, J.D. Mackenzie, *Ceramic Composites by the Sol-Gel Method*, Ceram. Eng. Sci. Proc., 14 (1993) 1-19.

38. J.D. Mackenzie, *Structures and Properties of Ormosils*, J. Sol-Gel Sci. and Tech., in press.

39. J.D. Mackenzie, *Recent Progress in Sol-Gel Science and Technology*, Proc. 3rd IUMRS, (1993) in press.

40. K. Morita, A. Makishima, *Ormosils and Effects of Ultrasonic Irradation*, Proc. 3rd IUMRS, (1993) in press.

41. J.D. Mackenzie, *Organically Modified Ceramics*, Proc. 3rd IUMRS (1993) in press.

42. E.M. Wong, H. Zheng, J.D. Mackenzie, T. Tsuchiya, *Ferromagnetic Cobalt Ferrite Films Prepared by the Sol-Gel Process*, MRS Symp. Proc., 313, in press.

43. C.H. Cheng, Y. Xu, J.D. Mackenzie, *The Growth of Epitaxial and Polycrystalline $KNbO_3$ Films via Sol-Gel Process*, Proc. 8th Int. Conf. on Ferroelectricity, 8-13 August, Gaithersburgh, MD, in press.

44. Y. Hu, Y.J. Chung and J.D. Mackenzie, *Synthetic Studies on the Gelation Process of an Organically Modified Silicate*, J. Mat. Sci., in press.

45. H. Park, H. Zheng, J.D. Mackenzie, *Ethanol Gas Sensing Properties of SnO_2-Based Thin Films*, Matls Letters, 17 (193) 376-352.

46. Y. Hu, C.H. Kanazawa, K. Morita, Y. Hoshina, J.D. Mackenzie, *Silicon Oxycarbide Fibers Drawn from an Organically Modified Silicate by Sol-Gel Method*, J. Sol-Gel Sci. and Tech. (1993) submitted.

47. Y. Hu, K. Morita, J.D. Mackenzie, *Preparation and Application of Ormosils by the Sol-Gel Method*, J. Sol-Gel Sci. and Tech. (1993) submitted.

48. K. Morita, Y. Hu, J.D. Mackenzie, *The Effects of Ultrasonic Irradiation on the Preparation and Properties of Ormosils*, J. Sol-Gel Sci. and Tech. (1993) submitted.

5. Educational and Professional Achievements

A great deal of the research carried out on this AFOSR-funded project has been performed by undergraduate and graduate students as laboratory assistants, respectively. During this period, a number of graduate students had received their M.S. and Ph.D. degrees through reseach performed under total or partial AFOSR support. Thus, the AFOSR research grant has been

invaluable in its educational impact. The majority of the students trained are now employed in research in industrial laboratotries and universities in this country.

a. M.S. Degree Recipients

F. Hulderman	February, 1991
Deanne Yamato	March, 1991
C.L. Tsai	June, 1991
Christine Kanazawa	September, 1991
Lisa Kao	September, 1991
T. Iwamoto	November, 1992
C. H. Cheng	September, 1992
Eva Wong	June, 1993
Justine Tseng	June, 1993
P. Lin	June, 1993

b. Ph.D. Degree Recipients

Mary Colby	September, 1991
C.J. Chen	July, 1992
Ren Xu	November, 1992
Young Chung	June, 1992
Y. Hu	July, 1993
C.Y. Li	November, 1993
C.J. Chu	November, 1993

c. Postdoctoral Scholars

H. Kozuka, Japan
K. Morita, Japan
Xu Yuhuan, China
F. Kirkbir, Turkey
H. Unuma, Japan
T. Takada, Japan

In October, 1991, Professor J.D. Mackenzie was one of 10 foreign scientists selected by the Japanese Ceramic Society to receive its Centenary Award in Yokohama, Japan. In May, 1991, Professor Mackenzie was elected

as a member of the International Academy of Ceramics for "Advancement of Ceramics Culture, Science and Technology." In July, 1992, Professor Mackenzie was the organizer and chairman of "Sol-Gel Optics II," an international conference sponsored by the S.P.I.E. at San Diego, CA. There were more than 200 attendees and Professor Mackenzie was the editor of the proceedings which were published in November, 1992. Dr. Xu Yuhuan was the author of a book, **Ferroelctric Materials and Their Applications**, published by North-Holland in 1991. Professor Mackenzie was elected as an Honorary member of the Japan Materials research Society in September, 1993.